

We claim:

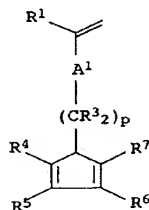
1. A supported catalyst for olefin polymerization comprising

A) as support material, a copolymer comprising at least the monomer units I, II and III,

where the monomer units I have the formula (I) and the monomer units II have the formula (II),



(I)



(II)

where the variables have the following meanings:

R¹ is hydrogen, C₁-C₄-alkyl or phenyl,

R² is substituted or unsubstituted aryl or branched or unbranched alkyl or alkenyl,

A¹ is a direct chemical bond or a substituted or unsubstituted phenylene group,

R³ are identical or different and are each hydrogen, C₁-C₁₀-alkyl or substituted or unsubstituted phenyl,

p is an integer from 0 to 8, and

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R^4 to R^7 are hydrogen, C_1 - C_{10} -alkyl or substituted or unsubstituted phenyl,

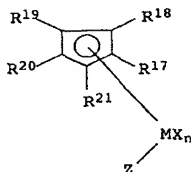
and the monomer units III have polar groups,

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and

B) at least one metallocene complex of the formula (V)

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(V)

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where the substituents and indices have the following meanings:

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M is titanium, zirconium, hafnium, vanadium, niobium, tantalum or chromium or an element of transition group III of the Periodic Table and of the lanthanides,

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X is fluorine, chlorine, bromine, iodine, hydrogen, C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical, $-OR^{22}$ or $-NR^{22}R^{23}$,

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n is 1, 2 or 3, where n corresponds to the valence of M minus 2,

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where

R^{22} and R^{23} are C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl, each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical and

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the radicals X are identical or different,

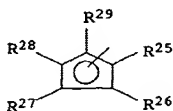
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R^{17} to R^{21} are hydrogen, C_1 - C_{10} -alkyl, 5- to 7-membered cycloalkyl which may in turn bear C_1 - C_{10} -alkyl groups as substituents, C_6 - C_{15} -aryl or arylalkyl, where two adjacent radicals may together form a saturated or unsaturated cyclic group having from 4 to 15 carbon atoms, or $Si(R^{24})_3$ where

R^{24} is C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl or C_6 - C_{15} -aryl and

Z is as defined for X or is



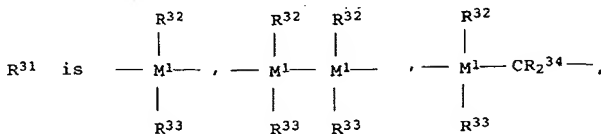
where the radicals

R^{25} to R^{29} are hydrogen, C_1 - C_{10} -alkyl, 5- to 7-membered cycloalkyl which may in turn bear C_1 - C_{10} -alkyl groups as substituents, C_6 - C_{15} -aryl or arylalkyl, where two adjacent radicals may together form a saturated or unsaturated cyclic group having from 4 to 15 carbon atoms, or $Si(R^{30})_3$ where

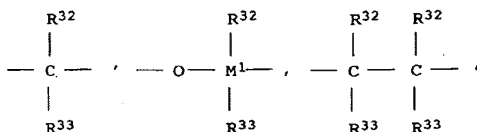
R^{30} is C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl or C_6 - C_{15} -aryl,

or the radicals R^{20} and Z together form an $-R^{31}-A-$ group where

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= BR³², = AlR³², -Ge-, -Sn-, -O-, -S-, = SO,
= SO₂, = NR³², = CO, = PR³² or = P(O)R³²,

where

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R³², R³³ and R³⁴ are identical or different and are each a hydrogen atom, a halogen atom, a C₁-C₁₀-alkyl group, a C₁-C₁₀-fluoroalkyl group, a C₆-C₁₀-fluoroaryl group, a C₆-C₁₀-aryl group, a C₁-C₁₀-alkoxy group, a C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl group, a C₈-C₄₀-arylalkenyl group or a C₇-C₄₀-alkylaryl group or two adjacent radicals together with the atoms connecting them form a saturated or unsaturated ring having from 4 to 15 carbon atoms, and

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M¹ is silicon, germanium or tin,

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A is -O-, -S-, $\begin{array}{c} \diagup \\ \diagdown \end{array} NR^{35}$ or $\begin{array}{c} \diagup \\ \diagdown \end{array} PR^{35}$,

where

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R³⁵ is C₁-C₁₀-alkyl, C₆-C₁₅-aryl, C₃-C₁₀-cycloalkyl, C₇-C₁₈-alkylaryl or Si(R³⁶)₃, where

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R³⁶ is hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl which may in turn bear C₁-C₄-alkyl groups as substituents or C₃-C₁₀-cycloalkyl,

or the radicals R²⁰ and R²⁸ together form an -R³¹- group

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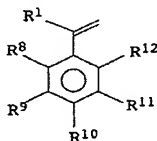
and

C) is at least one compound capable of forming metallocenium ions.

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2. A supported catalyst as claimed in claim 1, wherein the monomer units III are compounds of the formula (IIIa),

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(IIIa)

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where

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R⁸ to R¹² are hydrogen, C₁-C₁₀-alkyl, 5- to 7-membered cycloalkyl which may in turn bear C₁-C₁₀-alkyl groups as substituents, C₆-C₁₅-aryl or arylalkyl, or

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the radicals may together with adjacent radicals in each case form a saturated or unsaturated ring having from 5 to 15 carbon atoms,

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but at least one radical R⁸ to R¹² is a group of the formula (IV),

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IV

where

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R¹³ are identical or different and are each hydrogen, C₁-C₁₀-alkyl or substituted or unsubstituted phenyl,

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q is an integer from 0 to 8 and

$\frac{31}{6}$

A² is a group OR¹⁴, NR¹⁴R¹⁵, PR¹⁴R¹⁵, CN, COOR¹⁴ or
(O-(CH₂)_q)_{q'}-OR¹⁴, where R¹⁴ and R¹⁵ are identical
or different and are each hydrogen or C₁-C₄-alkyl
and q' is an integer from 1 to 5 and q'' is an
integer from 1 to 8,

or the monomer units III are compounds of the formula (IIIb),

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(IIIb)

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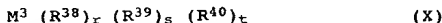
A³ is COOR¹⁶ or CN, where

R¹⁶ is hydrogen or C₁-C₁₀-alkyl.

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3. A supported catalyst as claimed in claim 1 or 2, wherein the
copolymer A) is crosslinked via the monomer units II.

4. A supported catalyst as claimed in any of claims 1 to 3 which
further comprises, as additional component D), one or more
metal compounds which are different from C) and have the
formula (X)



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where

M³ is an alkali metal, an alkaline earth metal or a
metal of main group III of the Periodic Table,
i.e. boron, aluminum, gallium, indium or thallium,

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R³⁸ is hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl or
arylalkyl each having from 1 to 10 carbon atoms in
the alkyl radical and from 6 to 20 carbon atoms in
the aryl radical,

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R³⁹ and R⁴⁰ are hydrogen, halogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl,
alkylaryl, arylalkyl or alkoxy each having from 1
to 10 carbon atoms in the alkyl part and from 6 to
20 carbon atoms in the aryl part,

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r is an integer from 1 to 3

and

5 s and t are integers from 0 to 2, where the sum $r+s+t$ corresponds to the valence of M^3 .

5. A supported catalyst as claimed in claim 4, wherein the copolymer A) serving as support material has been pretreated with compounds of the formula (X) prior to application of metallocene complex B) and compound C) capable of forming metallocenium ions.
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6. A process for preparing supported catalysts as claimed in any of claims 1 to 5, which comprises preparing copolymers comprising the monomer units I, II and III in solution or dissolving the copolymers in a suitable solvent after they have been prepared and adding the metallocene complex B) and the compound C) capable of forming metallocenium ions to this solution.
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7. A process for preparing supported catalysts as claimed in claim 6, wherein the copolymer A) is crosslinked at from 0 to 150°C by means of a Diels-Alder reaction either before or after the addition of metallocene complex B) and compound C) capable of forming metallocenium ions.
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8. A process for preparing supported catalysts as claimed in claim 6 or 7, wherein the copolymer A) is pretreated with compounds of the formula (X) prior to the addition of metallocene complex B) and compound C) capable of forming metallocenium ions.
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9. A copolymer which comprises the monomer units I, II and IIIa and is suitable as support material for catalysts for the polymerization of olefins.
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10. A process for the polymerization of olefins in the presence of a supported catalyst as claimed in any of claims 1 to 5.
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Supported catalyst for olefin polymerization

Abstract

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A supported catalyst for olefin polymerization comprises

A) as support material, a copolymer comprising the monomer units I, II and III,

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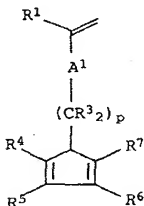
where the monomer units I have the formula (I) and the monomer units II have the formula (II),

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(I)

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(II)

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where the variables have the following meanings:

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R¹ is hydrogen, C₁-C₄-alkyl or phenyl,

R² is substituted or unsubstituted aryl or branched or unbranched alkyl or alkenyl,

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A¹ is a direct chemical bond or a substituted or unsubstituted phenylene group,

R³ are identical or different and are each hydrogen, C₁-C₁₀-alkyl or substituted or unsubstituted phenyl,

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p is an integer from 0 to 8, and

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R⁴ to R⁷ are hydrogen, C₁-C₁₀-alkyl or substituted or
unsubstituted phenyl,

and the monomer units III have polar groups,

5

and

B) at least one metallocene complex and

10 C) at least one compound capable of forming metallocenium ions.

A process for preparing such supported catalysts, copolymers
suitable as support material and a process for the polymerization
of olefins in the presence of a catalyst according to the present
15 invention are also provided.

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